ELECTRIC FIELD GRADIENTS AND NUCLEAR QUADRUPOLE RESONANCE IN POTASSIUMTETRAFLUOBORATE

G. PRABHAKARA SASTRY* AND J. RAMAKRISHNA**

PHYSICS DEPARTMENT, ANDHRA UNIVERSITY, WALTAIR, INDIA.

(*Received November* 19, 1968)

ABSTRACT. The electric field gradient tensor at the boron site in a single crystal of KBF_4 is calculated using the point charge model. Assuming the observed quadrupole coupling constant and the theoretical anti-shielding factor, it is found that the boron atom is nearly neutral and most of the negative charge of the BF_4^{-1} ion resides on the four fluorine atoms. Also, the asymmetry parameter and the orientation of the principal axes are calculated, which may prove useful in deciding which of the two available crystal structures is more accurate.

INTRODUCTION

We report here the results of our calculations on the boron nuclear quadrupole resonance in potassium tetrafluoborate, using the point charge model. The boron quadrupole coupling constant in KBF_4 was reported as 230 KC/S by Bray and Silver (1956). Due to the tetrahedral arrangement of the B–F bonds, there can be no contribution to the field gradient at the boron nucleus from the bonding electrons between boron and fluorine. This is also indicated by the small quadrupole coupling constant observed. The field gradient at the boron nucleus, therefore, arises directly from the charges on the neighbouring K^+ and BF^-_4 ions (Das and Hahn, 1958). Thus, the point charge model may be expected to give reliable results in this case.

The method of calculation is the same as the one described by Narasimha Rao and Narasimha Murty (1963). An arbitrary rectangular coordinate system *xyz* is chosen inside the crystal and the contributions to the field gradient at the site of interest due to all the neighbouring ions that make significant contributions, are evaluated ion after ion and a summation is made to obtain the field gradient tensor in the *xyz* system of reference. The field gradient tensor thus obtained is diagonalized to obtain the principal field gradient tensor, which is used to calculate the pure quadrupole resonance parameters.

* Present address : Physics Department, Indian Institute of Technology, Kharagpur, India.

** Physics Department, Michigan State University, East Lansing, U.S.A. Supported by a contract with the U.S. Atomic Energy Commission.

CRYSTAL STRUCTURE

The crystal structure of KBF_4 at room temperature is known to be orthorhombic. The space group is V_h^{16} (pnma) and the unit cell contains four molecules. At temperatures above 300°C, KBF_4 exhibits a simple cubic structure and in this phase the field gradient at the boron nucleus should vanish. However, the resonance in the higher phase has not yet been studied (Das and Hahn, 1958).

The BF_4^{-1} ion is a resonance hybrid of mainly five structures (Syrkin and Dyatkina, 1950) in which the charge on boron varies from $-1e$ to $+3e$ in steps of $1e$, where e is the proton charge, the contributions from the last two structures being small.

Two crystal structures were reported for KBF_4 (Structure Reports, 1950, and Wyckoff, 1961). They differ only in the unit cell dimensions and in the values of the atomic parameters. Otherwise, they are equivalent. The data given in Wyckoff (crystal structure II) gives a bigger tetrahedron for BF_4^{-1} than the data given in Structure reports (crystal structure I). The results of the present calculations point out that an experimental study of nuclear quadrupole resonance in this crystal may help to decide which of these crystal structures is more accurate.

RESULTS AND DISCUSSION

A. *Field Gradient Tensor*

Since KBF_4 is orthorhombic, the crystalline a, b, c axes are taken as the initial xyz system of reference with a boron atom at the origin. The potassium ion has a positive charge of $1e$, while BF_4 tetrahedron has a negative charge of $-1e$. The charge on boron is varied from $-1e$ to $+3e$ in accordance with the resonating structures of BF_4, and the remaining charge is distributed equally on the fluorines so that BF_4 has a net negative charge of $-1e$ in each case. The contributions to the field gradient tensor at the boron site, due to the surrounding ions are evaluated ion after ion and a summation is made to obtain the field gradient tensor in the initial xyz system of reference. The field gradient tensor thus obtained is diagonalized to obtain the principal field gradient tensor. It may be mentioned that most of the contribution to the z component of the field gradient tensor came from the fluorines of the BF_4 tetrahedron itself. The calculations have been performed in three steps : (1) Considering the nearest 50 neighbours in the structure reported in structure reports; (2) Considering the nearest 1,000 neighbours in the same crystal structure as above; (3) Considering the nearest 1,000 neighbours in the structure given in Wyckoff. In all the three cases, the quadrupole coupling constant came out to be more or less the same. This suggestions that the lattice sums converge over a very short range in this crystal, which is also pointed out by the fact that the four fluorines on the BF_4 tetrahedron contribute most of the field gradient.

For the case of crystal structure I, a zero charge on boron would result in a quadrupole coupling constant of 243 KC/S if only the nearest 50 neighbours are considered, and in a value of 300 KC/S if the nearest 1,000 neighbours are considered. For the case of crystal structure II, a zero charge on boron would result in a coupling constant of 190 KC/S. The smaller value in this case is not unexpected, because BF_4 tetrahedron is bigger in this case than in the former case. These values have to be compared with the experimental value of 230 KC/S and the agreement is satisfactory. As the other resonating structures of BF_4 with higher charges on boron are considered, the quadrupole coupling constant increases linearly with the charge on boron.

It may be mentioned that to get exact agreement with the observed quadrupole coupling constant, the charge on boron should be $-3e/10$ in the case of crystal structure I, and $+3e/8$ in the case of crystal structure II. This is due to the difference in the two crystal structures employed and points out the importance of knowing the lattice parameters accurately. Assuming a structure intermediate between the two considered here, it is easy to see that a charge of zero on boron would give right results.

B. *Asymmetry Parameter*

The value of the asymmetry parameter η is independent of the antishielding factor and gives a good indication of the accuracy of the crystal structue considered. The value of η in the case of crystal structure I is found to oscillate with the charge on boron, when only 50 neighbours are considered. But when the number of neighbours is increased to 1,000, the oscillations disappeared, leaving a value of 0·1 corresponding to zero charge on boron and a value of 0·16 corresponding to a charge of $-3e/10$ on boron. The crystal structure II gave a large value of 0·63 for zero charge on boron and a value of 0·8 for a charge of $+3e/8$ on boron. These results indicate that an experimental determination of η should point out which of the two crystal structures is more accurate.

C. *Orientation of Principal Axes*

According to crystal structure I, the principal Z direction lies in the ac plane making an angle of 54°27′ with the a axis. The principal y direction is along the $-b$ direction. Crystal structure II does not yield the same results. It gives the principal z axis in the bc plane nearly along the b axis. The principal y axis is nearly in the ac plane making an angle fo 2° with the plane and 12° with the c axis. Thus again, experimental determination of the orientation of the principal axes also should help to decide which of the two crystal structures is more accurate.

D. *Discussion and Conclusions*

In view of the small coupling constant, and the tetrahedral arrangement of the B–F bonds, we believe that the point charge model would yield resonable

results in this case. We realize that the charge distribution in complex groups like BF_4 cannot be adequately described simply by placing fractional charges on the atoms in the group. Despite this limitation, the present calculations should help to decide between the two available crystal structures, once the experimental values of η and the orientation of principal axes become available.

REFERENCES

Das, T. P. and E. L. Hahn, 1958, *Nuclear Quadrupole Resonance Spectroscopy*, Academic Press, Inc., p. 188.

Narasimha, Rao D. V. G. L. and Murty A. Narasimha, 1963, *Phys. Rev.*, **132**, 961.

Structure Reports, 1950, **13**.

Syrkin, Y. K. and Dyatkina, N. E., 1950, *Structure of Molecules and the Chemical Bond*, Interscience Publishers, Inc., New York, p. 110.

Wyckoff, R. W. G., 1961, *Crystal Structures*, Vol. I.